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Japanese Published Unexamined (Kokai Koho) Patent Application (A) No. 02-069525, published March 8, 1990; Application No. 63-221971, filed September 5, 1988; Int.: C 08 G 73/00, C 23 C 30/00; Inventor(s): Masao Abe et al.; Assignee: Nitto Electric Engineering, Inc.; Japanese Title: Conductive Organic Polymer Thin Film Composite Body and Manufacturing Method Therefor

**CONDUCTIVE ORGANIC POLYMER THIN FILM COMPOSITE BODY
AND MANUFACTURING METHOD THEREFOR**

CLAIM(S)

1) A conductive organic polymer thin film composite body, which is expressed by the following formula (T. Note: The formula is attached to the end of the translation), and is virtually made of linear polymer having repeated units of quinonediimine structure, and wherein conductive organic polymer having conductivity 10^{-6} S/cm or more is formed on a substrate in form of thin film, characterized in that it contains polymer acid as a dopant.

2) A conductive organic polymer thin film composite body, which is composed of linear polymer having repeated units of quinonediimine structure expressed by the aforementioned formula that is produced by chemically polymerizing aniline or its derivative by oxidation by using an oxidant having the standard electrode potential 0.6 V or higher defined as an electromotive force for a reducing half-cell battery reaction using the standard hydrogen electrode as a reference,

characterized in that polymer acid is used as a dopant when the conductive organic polymer having the conductivity 10^{-6} S/cm or higher is deposited on said substrate in thin film form.

DETAILED DESCRIPTION OF THE INVENTION

(Field of Industrial Application)

The present invention pertains to a conductive organic polymer thin film composite body and manufacturing method thereof, more specifically, to a conductive organic polymer thin film composite body having polymer acid as a dopant, wherein a conductive organic polymer is deposited in thin film form on a substrate.

(Prior Art)

There is a publicly known method to manufacture conductive organic polymer containing electrolytic ions as a dopant and having conductivity 10^{-6} S/cm, wherein aniline or its derivative is chemically polymerized by oxidization with an oxidant in the presence of proton acid. The electrolytic ions used as said dopant is anion derived from the proton acid used.

Also, Japanese Unexamined Patent Application 61-266435 discloses that a conductive organic polymer thin film can be formed on the surface of a substrate by polymerization by oxidation.

(Problems of the Prior Art to Be Addressed)

The inventors, after having studied on the composite body, wherein a conductive organic polymer thin film made of oxidized polymer of aniline or its derivative is deposited on a substrate, found that by using polymer acid as a dopant, the manufactured conductive organic polymer thin film can be improved to be stronger and more adhesive to the substrate, and realized the present invention.

(Means to Solve the Problems)

The conductive organic polymer thin film composite body of the present invention is expressed by the following formula [T. Note: The formula is attached to the end of translation.] and is composed of linear polymer having repeated units of quinonediimine structure. In this composite body, the conductive organic polymer having conductivity 10^{-6} S/cm or more is formed on a substrate in form of thin film and has polymer acid as a dopant.

The conductive organic polymer thin film composite body of the present invention is composed of linear polymer having repeated units of quinonediimine structure expressed by the aforementioned formula that is produced by chemically polymerizing aniline or its derivative (hereinafter called monomer) by oxidation by using an oxidant having the standard electrode potential 0.6 V or higher, which is defined as an electromotive force for a reducing half-cell battery reaction that uses

the standard hydrogen electrode as a reference, and it can be manufactured by using polymer acid as a dopant when the conductive organic polymer having the conductivity 10^{-6} S/cm or higher is deposited on said substrate in form of thin film.

More specifically, monomer is added to a reaction medium containing polymer acid, and is agitated; polymer acid and salt are dissolved in the monomer and the oxidant is added to it in form of liquid or solid to polymerize the monomer by oxidation.

As to said monomer, aniline is preferred. As to the derivative, alkyl aniline, such as 0-methyl aniline, m-methyl aniline, 0-ethyl aniline, or m-ethyl aniline, is preferred.

The polymer acid used in the present invention is polymer acid with strong acidity having pka value 3 or less. When polymer acid having pka value 3 or higher is used, the oxidized polymer produced from the monomer cannot be doped. As to the polymer acid preferably used in the present invention, for example, the following can be cited: polystyrene sulfonate; polyvinyl sulfate; polyvinyl sulfonate; polyaryl sulfonate; polymethacryl sulfonate; poly(2-methyl-2-acrylamide propane sulfonate).

As to the reaction medium, water is generally used, but if necessary, an organic solvent is used. When an organic solvent is used, it needs to be the solvent

that is not oxidized by an oxidant used for the reaction. As to the organic solvent, for example, acetone, tetrahydrofuran, and acetic acid can be cited.

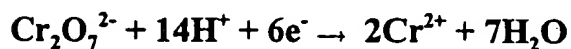
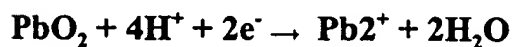
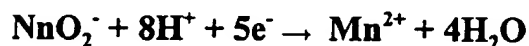
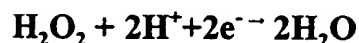
The oxidant used in the present invention has the standard electrode potential 0.6 V or higher, which is defined as an electromotive force for a reducing half-cell battery reaction that uses the standard hydrogen electrode as a reference. If the oxidant is water-soluble, it needs to be neutral, and it should not produce anionic salt after having been reduced. More specifically, in the oxidation reaction of the polymer, the oxidant is reduced but should not produce anionic seeds. The conductive organic polymer produced by said polymerization by oxidation contains a π -electron conjugate group, which is partially oxidized and forms a site having positive electrons. When the oxidant produces anion seeds, said anion seeds are captured by said site, and said anion seeds constitute a dopant together with polymer acid; thus the conductive organic polymer thin film having only the desired polymer acid as a dopant can be produced.

As to the oxidant used in the present invention, it needs to have an oxidization capability to polymerize the polymer by oxidation, and such an oxidant, as is disclosed in Japanese Unexamined Published Application No. 61-258831, needs to have the standard electrode potential 0.6 V or higher, which is defined as an electromotive force for a reducing half-cell battery reaction that uses the standard

hydrogen electrode as a reference. In the method of the present invention, if the proton interferes with the reduction half-cell reaction, as in $\text{Cr}_2\text{O}_7^{2-}$, the standard electrode potential in the reaction with which the proton interferes is used as the standard electrode potential. This standard electrode potential is described in "CRC Handbook of Chemistry and Physics" (CRC Press, Inc., D-155-D-160) or "Directory of Electrochemistry" by Electrochemical Society (Maruzen, Inc., pp. 71-74).

As to the oxidant that meets the above two conditions, any of the following can be used: hydrogen peroxide; permanganate; lead dioxide; bichromate; manganese dioxide.

These oxidants do not produce anionic seeds after having been reduced as shown below.



Said oxidant is preferably used by the equivalent amount to the amount of monomer to be polymerized by oxidation. If the amount exceeds said equivalent

amount, the excessive oxidant will remain in the reaction system. If an oxidant that does not produce anionic seeds after having been reduced by oxidation is used, it may contain anionic seeds.

As to the polymer acid to be used, its acid radical mol weight is preferred to be mol weight of the monomer. If the acid radical mol weight of the polymer acid is less than the mol weight of the monomer, the excessive amount of the monomer does not form the polymer acid and salt. If a water reaction medium is used, separation occurs in oily form, and is not desirable. Generally speaking, if the polymer acid amount is more than the monomer amount, the polymer produced has high conductivity.

The reaction temperature is not limited to a specific degree, as long as it is lower than the boiling point of the solvent. As the reaction temperature gets higher, the conductivity of the produced oxidized polymer gets lower, so a normal temperature or lower is preferred in order to produce the polymer with high conductivity.

The point to be noted in the present invention is to place a substrate in the reaction chamber before or after the polymerization of the polymer by oxidation. Therefore, if an oxidant is gradually added to the monomer solution for polymerization by oxidation, the substrate needs to be immersed in the monomer

solution before the oxidant is added, or the substrate can be immersed in the monomer solution during the induction period before the polymerization begins. More preferably, the substrate is immersed in the monomer solution immediately after the oxidant is added. In other words, the substrate is immersed during the induction period before the polymer is actually deposited in the reaction chamber and the monomer is colored. The induction period varies depending on the oxidant used. If the substrate is immersed in the reaction chamber after the polymer actually begins to be deposited, a thin film of the conductive organic polymer will not be formed on the substrate or will be partially formed, so a uniform thin film cannot be formed on the substrate.

The substrate to be used in the present invention is not limited to a specific type, but the following can be cited: glass, ceramic or porous film; isotropic or anisotropic organic polymer sheet or film; non-woven or woven cloth; metal or semiconductor mold or sheet. The shape of the substrate is not limited to a specific shape. For example, other than the aforementioned sheet or film, a cake- or fiber formed substrate, various molds or hollow mold can be used as the substrate. By the present invention, said conductive organic polymer thin film can be formed on the surface of the substrate that contacts with the reaction medium.

If an alloy is used for the substrate, the conductive organic polymer thin film

such as a vapor deposition film can be used. In such a case, however, an alloy that is not oxidized by an oxidant in the reaction system needs to be selected. Thus, by the present invention, the conductive organic polymer thin film can be formed on an insulated substrate. The conductive organic polymer thin film thus formed on the substrate generally has some micron thickness. In the method of the present invention, the polymer is deposited on the substrate in form of thin film after a few minutes to a few hours of induction period following the addition of the oxidant. After the reaction, it may be set aside for a few minutes to a few hours for maturing. Subsequently, the substrate on which the polymer thin film is formed is removed, washed, rinsed with an organic solvent if necessary, and vacuum-dried to produce the conductive organic polymer thin film composite body.

As explained above, the conductive organic polymer thin film composite body of the present invention is virtually composed of linear polymer having the repeated units of quinonediimine expressed by the aforementioned formula, wherein the conductive organic polymer having the conductivity 10^{-6} S/cm or higher contains polymer acid as a dopant used at the time of polymerization, and the conductive organic polymer has a green or greenish black color.

Moreover, in the conductive organic polymer thin film composite body of the present invention, the conductive organic polymer is doped with polymer acid, and

both are strongly bonded. With the conductive organic polymer having low mol anion as a dopant, the dopant is easily dissociated from the polymer by undoping, but with the composite body of the present invention, the polymer acid is not dissociated from the organic polymer by undoping treatment.

(Advantage)

As explained above, the conductive organic polymer thin film composite body of the present invention is, for its having polymer acid as its dopant, mechanically more excellent, more adhesive to the substrate, as compared to the prior art composite body having low mol anion as a dopant, therefore, is applicable to various uses as the conductive organic material.

For example, the polymer thin film formed on an inert metal, such as platinum or gold, can be a Schottky junction device if a metal such as indium is bonded by vapor deposition. The composite body, in which the conductive organic polymer thin film is formed on the silicon semiconductor, can be used as a hetero-junction device.

The composite body, in which the conductive organic polymer thin film is formed on the resin film, can be used as a polarized optical device combined with an electromagnetic shielding material, reflection preventing film, optical filter element, and with a drawn resin film. It is also applicable to a thin film type plastic battery

or solar battery.

(Embodiment Example)

The present invention is explained below with reference to the embodiment example and reference example. But the present invention is not limited to this embodiment example.

(Reference Example)

(Synthesis of Polyaryl Sulfone)

Into a separable flask with 300 ml capacity equipped with an agitator, cooler, nitrogen introducing pipe, thermometer and monomer inlet, 20 g of distilled water and 0.33 g of 2,2' - azo bis {2-methyl-N (1.1 - bis [hydroxyl methyl] ethyl) propione amido} as a radical polymer initiation agent were added and dissolved at 60°C. After nitrogen is blown into it for 10 minutes, 64 g of sodium arylsulfonate was gradually added, and dissolved at 90°C by heating by a mantle heater.

After the entire amount of said sodium aryl sulfonate was dissolved, nitrogen was blown into it again for 10 minutes. Then, the polymerization was performed in the presence of nitrogen flow at 100°C for 6.5 hours.

After it was set aside at a normal temperature overnight, 80 g of distilled water was added, agitated, and the entire amount was put into methanol 1600 ml; thus a white sediment was produced. This white powder was filtered through a glass

filter, vacuum dried at 80°C for 7 hours; thus 20.5 g of polyarylsulfonate was produced. The polymerization rate was 32.0 %.

The logarithmic viscosity measured in water at 30°C and 0.5 g/dl concentration was 0.052 dl/g. The logarithmic viscosity mol weight (polyethylene glycol conversion) by CPC 2200 and Mw/Mn was 1.07.

This sodium polyaryl sulfonate 12 g was dissolved in 48 g of distilled water to prepare 20 weight% solution. A glass column charged with an H type strong acidic cationic exchange resin "Dowex 50 W-X12" (Dow Chemical Corporation) was thoroughly washed with distilled water, and after confirming that the effluent became neutral, said sodium polyaryl sulfonate solution was supplied to the column by a metering pump; the effluent began to be collected at the point when it was changed to acidic; distilled water was put through the column; and the effluent was continuously collected until it became almost neutral.

When a portion of the collected effluent was put to titration by a 0.01 N sodium hydroxide solution, the polymer concentration in the effluent was 0.32 mol/l; thus 186 ml of polyaryl sulfonate solution was produced.

(Embodiment Example 1)

Into 15 ml of polyaryl sulfonate solution with 0.32 mol/l concentration, 0.45 g of aniline was dissolved. This was defined as an A solution. Separately, into the

same polyaryl sulfonate solution 50 ml, 0.406 g of ammonium dichromate was dissolved. This is defined as a B solution.

Into a glass petri dish with a 9 cm diameter, a slide glass sheet, nesa glass sheet, polyethylene terephthalate film, ITO transparent conductive film and n-type silicon wafer were placed as a substrate. Said A solution and B solution cooled by ice water were mixed and poured into the petri dish while the petri dish was being cooled by ice water. The color of the pink colored mixed liquid began to be changed to greenish brown, bluish black, and greenish black, and the reflected light on the liquid surface changed from purple to greenish black.

After the substrate was set aside for 18 hours, it was removed from the conductive polymer produced in the petri dish and was washed with distilled water and with acetone in this order, vacuum-dried in deccicater for 5 hours; thus, the conductive organic polymer thin film composite body of the present invention was manufactured.

The thin film formed on the polyethylene terephthalate film was 2 μm . FT-IR spectrum of this polymer thin film measured by a KBr method is shown in Fig. 1.

The conductivity of the conductive organic polymer thin film formed on the slide glass sheet was measured by 3 points. The result was: 0.23 S/cm; 0.29 S/cm; 0.19 S/cm. On the nesa glass sheet, ITO transparent conductive film and on n-type

silicon wafer, the greenish black conductive organic polymer thin film was deposited, likewise. These thin films were not fallen off or peeled from the substrate when distilled water was jetted out powerfully from a washing bottle, so they were proved to have excellent adhesion.

(Embodiment Example 2)

By using the same amounts of A solution and of ammonium dichromate as those in Embodiment Example 1, and 38 ml, 25 ml and 13 ml of polyaryl sulfonate solutions of B solution (The mol ratio of sulfonate radical of polyaryl sulfonate to ammonium dichromate is 7.5, 5, and 2.5, respectively.), the conductive organic polymer thin film was deposited on the slide glass as in Embodiment Example 1. The conductivities of the conductive organic polymer thin films thus manufactured were 0.37 S/cm, 7.6×10^{-2} S/cm and 9.2×10^{-4} S/cm, respectively.

(Embodiment Example 3)

Sodium vinyl sulfonate was put to radical polymerization by a potassium peroxydisulfate/sodium bisulfate redox initiation agent at a normal temperature, and produced sodium polyvinyl sulfonate. The logarithmic viscosity of this polymer measured in water at 30°C and at 0.5 g/dl concentration was 0.20dl/g. By ion-exchanging this polymer, polyvinyl sulfonate was produced.

At 10 times the mol ratio of polyvinyl sulfonate to ammonium dichromate, 2

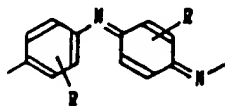
μm thick conductive organic polymer thin film was deposited on the slide glass, as in Embodiment example 1. The conductivity of this thin film was 0.15 S/cm. The adhesion of the thin film to the substrate was excellent.

Comparison Example

In place of polyaryl sulfonate, hydrochloric acid was used. As in Embodiment Example 1, the conductive organic polymer containing hydrochloric acid as a dopant was deposited on the slide glass up to 1 μm . The conductivity of this thin film was 3.5×10^{-6} S/cm. When distilled water was jetted out of a washing bottle to this thin film, the thin film was cracked and peeled off from the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the FT -IR spectrum of the polymer thin film in the conductive organic polymer thin film composite body of the present invention that was measured by a Kbr method.



(In the formula, R indicates hydrogen or alkyl radical)